

# KIITEE Chemistry Sample Paper – 3

Duration: 50 Minutes

Maximum Marks: 160

## Instructions

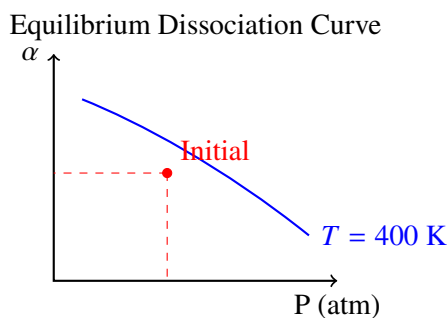
- This paper contains **40** Multiple Choice Questions (Single Correct Answer), modelled on the Chemistry portion of **KIITEE** entrance.
- Each correct answer carries **+4 marks**. There is **-1 mark per wrong answer**; unattempted questions score **0**
- Only **one** option is correct. Choose carefully.
- Syllabus level: **Class 11 12 (10+2) Chemistry — Organic Chemistry, Physical Chemistry, Inorganic Chemistry, Environmental Chemistry, Polymers Biomolecules**
- The test is computer based. Personal calculators, log tables, mobile phones, and other electronic gadgets are strictly prohibited.

**Q1.** The esterification of benzoic acid with (R)-1-phenylethanol in the presence of dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP) produces an ester. The stereochemical configuration at the chiral carbon of the ester formed is:

- (A) (S)-configuration (inverted)
- (B) (R)-configuration (retained)
- (C) Racemic mixture
- (D) Meso compound

**Q2.** For the reaction  $N_2O_4 \rightleftharpoons 2NO_2$ , the equilibrium can be shifted by varying temperature and pressure. If the system initially at equilibrium at 400 K and 2 atm is compressed isothermally, the degree of dissociation of  $N_2O_4$  will:





- (A) Increase
- (B) Decrease
- (C) Remain unchanged
- (D) First increase then decrease

**Q3.** The complex  $[Cu(NH_3)_4]^{2+}$  exhibits a d-d absorption band around 610 nm, producing a blue colour. The d-electron configuration and the ground state term symbol for Cu(II) are:

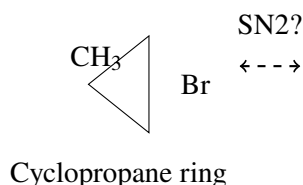
- (A)  $d^9, {}^2D_{5/2}$
- (B)  $d^{10}, {}^1S_0$
- (C)  $d^9, {}^2D_{3/2}$
- (D)  $d^8, {}^3F_4$

**Q4.** Persistent organic pollutants (POPs) such as DDT bioaccumulate in aquatic food chains. Which of the following structural features of DDT makes it highly persistent in the environment?

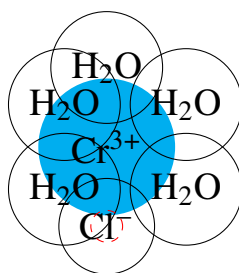
- (A) Presence of multiple hydroxyl groups
- (B) Presence of multiple C-Cl bonds with high bond dissociation energy
- (C) Presence of ester linkages susceptible to hydrolysis
- (D) Presence of primary amine groups

**Q5.** The  $S_N2$  displacement of (S)-1-bromo-1-methylcyclopropane with cyanide ion is known to be extremely slow. The reason for this unusual reactivity pattern is:





- (A) Weak C-Br bond that breaks spontaneously
- (B) Steric hindrance from the cyclopropane ring preventing back-side attack
- (C) High electronegativity of Br atom
- (D) Conjugation with aromatic ring
- Q6.** A reversible reaction  $A(g) + B(g) \rightleftharpoons C(g)$  reaches equilibrium at 500 K. The reaction has  $\Delta H = -20$  kJ/mol. To maximize the yield of product C at equilibrium, a chemist should:
- (A) Increase temperature
- (B) Decrease temperature
- (C) Increase only the concentration of A
- (D) Maintain temperature and increase total pressure
- Q7.** In the coordination compound  $[Cr(H_2O)_6]^{3+}$ , if one water molecule is replaced by a chloride ion to form  $[Cr(H_2O)_5Cl]^{2+}$ , the crystal field splitting parameter ( $\Delta_o$ ) will:



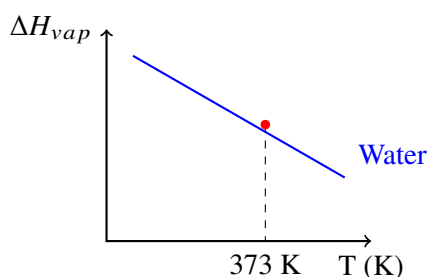
- (A) Increase ( $Cl^-$  is a stronger field ligand than  $H_2O$ )
- (B) Decrease ( $Cl^-$  is a weaker field ligand than  $H_2O$ )
- (C) Remain unchanged
- (D) Unpredictable without experimental data



**Q8.** In the alkaline hydrolysis of esters (saponification), the reaction is essentially irreversible. This is because:

- (A) The carboxylate anion formed is stabilized by resonance and does not re-esterify easily
- (B) The reaction produces water which shifts the equilibrium forward
- (C) The alcohol is a better nucleophile than hydroxide ion
- (D) The reaction rate is extremely slow in the reverse direction

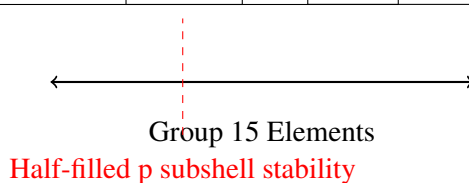
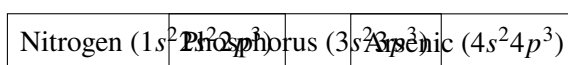
**Q9.** The enthalpy of vaporization of a liquid varies with temperature. At the normal boiling point ( $100^{\circ}\text{C}$  for water), the relationship between  $\Delta H_{vap}$  and the clausius-Clapeyron equation predicts that as temperature increases further,  $\Delta H_{vap}$  will:



- (A) Increase
  - (B) Decrease
  - (C) Remain constant
  - (D) Become negative
- Q10.** The hydration of alkenes can proceed via two mechanistic pathways: (1) acid-catalyzed hydration (Markovnikov's rule), and (2) oxymercuration followed by reduction. Comparing these two methods, which statement is accurate?
- (A) Both methods always produce the same product in the same proportion
  - (B) Acid-catalyzed hydration can produce rearranged products via carbocation shifts, while oxymercuration prevents rearrangement
  - (C) Oxymercuration is faster but produces only racemic mixtures
  - (D) Acid-catalyzed hydration produces more thermodynamically stable products



- Q11.** Natural rubber (cis-polyisoprene) can be vulcanized by heating with sulfur to improve its mechanical properties. The vulcanization process creates which type of cross-links between polymer chains?
- (A) Hydrogen bonds  
 (B) Ionic bonds  
 (C) Disulfide bonds (C-S-S-C and C-S-C cross-links)  
 (D) Peptide bonds
- Q12.** The synthesis of primary amines from alkyl halides via the Gabriel synthesis avoids over-alkylation because:
- (A) The phthalamide anion is stabilized by two carbonyl groups, making it a poor nucleophile for secondary attack  
 (B) The primary amine produced immediately precipitates out of solution  
 (C) The reaction is catalyzed by Lewis acids that become saturated after one nucleophilic displacement  
 (D) Phthalamide decomposes after the first nucleophilic attack
- Q13.** For a colloidal dispersion, the Tyndall effect is observed due to:
- (A) Scattering of light by colloidal particles (size 1-1000 nm) which is intermediate between solution and suspension  
 (B) Complete absorption of light by the colloidal particles  
 (C) Reflection of light from the surface of the container  
 (D) Refraction of light through a gradient of refractive indices
- Q14.** The first ionization energy of group 15 elements shows an anomalous trend: the value for phosphorus is greater than that of sulfur (even though sulfur is to the right). The best explanation for this is:



- (A) The half-filled  $p^3$  orbital configuration of P is particularly stable
- (B) Phosphorus has a larger atomic radius than nitrogen
- (C) The 3p orbital of P is more diffuse than the 2p orbital of N
- (D) Sulfur has filled d orbitals that provide better shielding

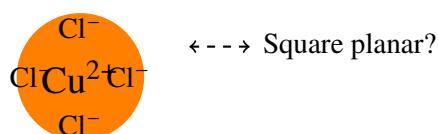
**Q15.** In a kinetically controlled reaction, the major product formed is the one with the lowest activation energy, not the lowest free energy. Which statement correctly illustrates kinetic control?

- (A) Formation of para-disubstituted benzene in electrophilic aromatic substitution at room temperature (thermodynamic product)
- (B) Formation of 1,2-addition product at low temperature in a diene reaction (kinetic product dominates)
- (C) Formation of the most stable enol tautomer in acidic conditions
- (D) Formation of the most stable carbanion intermediate in strong base

**Q16.** The solubility product ( $K_{sp}$ ) of  $Mg(OH)_2$  is  $1.8 \times 10^{-11}$  at  $25^\circ\text{C}$ . If a saturated solution of  $Mg(OH)_2$  has a pH of 10.5, the molar solubility of  $Mg(OH)_2$  is approximately:

- (A)  $1.4 \times 10^{-4}$  M
- (B)  $1.8 \times 10^{-5}$  M
- (C)  $3.6 \times 10^{-4}$  M
- (D)  $9.0 \times 10^{-6}$  M

**Q17.** The geometry of the  $[CuCl_4]^{2-}$  complex is square planar rather than tetrahedral. This preference arises from:



- (A) The  $d^9$  configuration of Cu(II) undergoes Jahn-Teller distortion to relieve electronic strain



- (B) The  $d^8$  configuration of Cu(I) prefers square planar geometry
- (C) The chloride ligand induces a tetrahedral geometry which then spontaneously distorts
- (D) The square planar geometry maximizes ionic bonding strength

**Q18.** In the ozonolysis of an alkene, the initial adduct (primary ozonide) is unstable and rearranges to a secondary ozonide. The mechanism involves:

- (A) A 1,3-dipolar cycloaddition followed by a retro-cycloaddition and recombination
- (B) A direct  $S_N2$  displacement of oxide groups
- (C) An  $S_N1$  mechanism involving carbocation intermediates
- (D) A free radical chain propagation mechanism

**Q19.** At constant volume, when a mixture of gases is heated from 273 K to 546 K, the pressure is expected to approximately:

- (A) Double (Gay-Lussac's Law:  $P_1/T_1 = P_2/T_2$ )
- (B) Remain unchanged
- (C) Halve
- (D) Increase by a factor of 4

**Q20.** The carbonic acid ( $H_2CO_3$ ) in aqueous solution is in equilibrium with dissolved  $CO_2$  and water. The primary species present in solution at pH 7 is:

- (A)  $H_2CO_3$  (molecular form)
- (B)  $HCO_3^-$  (bicarbonate ion)
- (C)  $CO_3^{2-}$  (carbonate ion)
- (D)  $CO_2(aq)$  (dissolved gas)

**Q21.** In the preparation of phenol from benzene, the cumene (isopropylbenzene) oxidation process involves formation of a hydroperoxide intermediate. The acid-catalyzed decomposition of this hydroperoxide produces both phenol and acetone. This route is industrially preferred because:

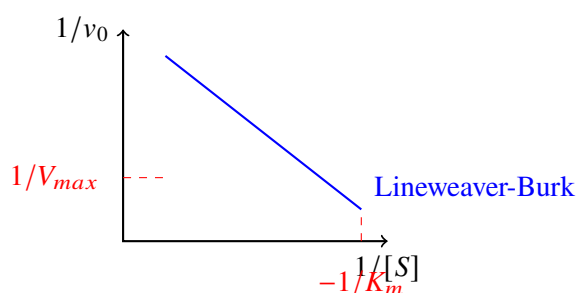


- (A) It produces phenol with higher purity than direct hydroxylation
- (B) The co-product acetone has significant commercial value
- (C) It avoids the use of toxic chlorine gas
- (D) It allows for complete recycling of unreacted starting material

**Q22.** The dipole moment of water ( $\mu = 1.85$  D) is significantly lower than the vector sum of the individual H-O bond dipoles. This indicates:

- (A) The O-H bonds are non-polar
- (B) Partial cancellation of individual bond dipoles due to the bent molecular geometry
- (C) The molecule is optically inactive
- (D) There is no electronegativity difference between H and O

**Q23.** In the kinetics of enzyme catalysis, the Lineweaver-Burk plot (double reciprocal plot) is a linearization of the Michaelis-Menten equation. The intercept and slope of this plot provide information about:



- (A) y-intercept =  $1/V_{max}$  and x-intercept =  $-1/K_m$
- (B) y-intercept =  $K_m$  and slope =  $V_{max}$
- (C) Slope =  $1/V_{max}$  and y-intercept =  $K_m/V_{max}$
- (D) All parameters are determined solely from the slope

**Q24.** In the synthesis of urea via the Haber-Bosch process followed by carbon dioxide reaction, ammonia and carbon dioxide combine at high temperature and pressure. The reaction is:

- (A)  $2NH_3 + CO_2 \rightarrow NH_2COONH_4$  (ammonium carbamate, intermediate)



- (B)  $N_2 + O_2 \rightarrow NO$  (nitrogen fixation step)
- (C)  $NH_3 + CO_2 \rightarrow$  urea (direct one-step conversion)
- (D)  $NH_3 + HNO_3 \rightarrow NH_4NO_3$  (nitrate formation)

**Q25.** The Hofmann elimination reaction converts quaternary ammonium salts into alkenes and tertiary amines. The reaction is anti-periplanar (E2 mechanism) and produces:

- (A) The major alkene product following Zaitsev's rule (most substituted alkene)
- (B) The minor alkene product (least substituted alkene, Hofmann product)
- (C) A mixture of syn and anti addition products
- (D) A carbocation intermediate rearrangement product

**Q26.** The surface area of adsorbent material significantly influences adsorption capacity. In industrial applications like water purification with activated carbon, the high surface area (up to 3000 m<sup>2</sup>/g) is achieved by:

- (A) Creating a microporous and mesoporous internal structure
- (B) Using a single large surface rather than fragmented pieces
- (C) Coating the adsorbent with metallic compounds
- (D) Maintaining the adsorbent at very low temperatures

**Q27.** The electrode potential of the  $Fe^{3+}/Fe^{2+}$  couple is  $E = +0.77$  V, while for the  $I_2/I^-$  couple it is  $E = +0.54$  V. A solution containing both  $Fe^{3+}$  and  $I^-$  ions will undergo spontaneous reaction to produce:

- (A)  $Fe^{2+}$  and  $I_2$  ( $Fe^{3+}$  oxidizes  $I^-$  to  $I_2$ )
- (B)  $Fe^{3+}$  and  $I^-$  (no reaction, system is stable)
- (C)  $Fe^{2+}$  and  $I^-$  ( $I^-$  is oxidized instead)
- (D) A mixture of  $Fe^{2+}$ ,  $Fe^{3+}$ ,  $I^-$ , and  $I_2$  at constant concentrations

**Q28.** In the nomenclature of alkynes, the triple bond takes priority in numbering the carbon chain. For the compound  $HC \equiv C - CH_2 - CH(CH_3)_2$ , the IUPAC name is:



- (A) 1-ethyl-3-methylpropyne
- (B) 3-methylbut-1-yne
- (C) 4-methylpent-1-yne
- (D) 2,2-dimethylpropyne

**Q29.** In the Born-Haber cycle for ionic crystal formation, the step that requires the most energy input is typically:

- (A) Ionization energy of the metal atom
- (B) Lattice enthalpy of the ionic crystal (breaking apart the solid)
- (C) Electron affinity of the non-metal
- (D) Sublimation energy of the metal

**Q30.** The  $[\text{PtCl}_4]^{2-}$  ion exhibits strong absorption bands in the UV-visible region due to:

- (A) Metal-to-ligand charge transfer (MLCT) transitions
- (B) d-d transitions within the d-electron manifold of Pt(II)
- (C) Ligand-to-metal charge transfer (LMCT) transitions
- (D) Spin-flip excitations from singlet to triplet states

**Q31.** In the reduction of carboxylic acids to primary alcohols, lithium aluminum hydride ( $\text{LiAlH}_4$ ) is significantly more reactive than sodium borohydride ( $\text{NaBH}_4$ ). The reason is:

- (A) The Al-H bond in  $\text{LiAlH}_4$  is more polar and delivers hydride more effectively than the B-H bond in  $\text{NaBH}_4$
- (B) Lithium is a more reactive metal than sodium
- (C)  $\text{LiAlH}_4$  can react with water, making it more aggressive as a reducing agent
- (D)  $\text{NaBH}_4$  forms a stable complex with carboxylic acids

**Q32.** According to VSEPR theory, the molecular geometry of  $\text{XeF}_5^+$  (xenon pentafluoride cation) is:



- (A) Square pyramidal
- (B) Trigonal bipyramidal
- (C) Tetrahedral
- (D) Pentagonal planar

**Q33.** The coordination chemistry of iron(II) is dominated by octahedral geometry. In the complex  $[Fe(CN)_6]^{4-}$ , the cyanide ligand is:

- (A) A strong field ligand causing large crystal field splitting, resulting in a low-spin (diamagnetic) complex
- (B) A weak field ligand causing small crystal field splitting, resulting in a high-spin (paramagnetic) complex
- (C) A bidentate chelating ligand
- (D) Incapable of stabilizing Fe(II) due to incompatible  $d$  orbital symmetry

**Q34.** In the atmosphere, the anthropogenic increase in greenhouse gas concentrations leads to climate change. The gas that contributes most to the greenhouse effect is:

- (A) Carbon dioxide ( $CO_2$ ) due to high atmospheric concentration and long residence time
- (B) Methane ( $CH_4$ ) due to high global warming potential (GWP) over 20-year period
- (C) Nitrous oxide ( $N_2O$ ) due to catalytic ozone depletion
- (D) Ozone ( $O_3$ ) due to strong absorption in the infrared region

**Q35.** The decomposition of hydrogen peroxide ( $H_2O_2$ ) is catalyzed by the enzyme catalase. The reaction mechanism involves formation of an enzyme-substrate complex. The Michaelis constant ( $K_m$ ) represents:

- (A) The substrate concentration at which the reaction rate is half of  $V_{max}$
- (B) The dissociation constant of the enzyme-substrate complex
- (C) The rate constant for product formation



(D) The total enzyme concentration in the reaction

**Q36.** In the electrolysis of aqueous copper sulfate solution using copper electrodes, the products at the cathode and anode are:

(A) Cathode: Cu metal; Anode: Oxygen gas (pure copper anode case) or Cu metal dissolution (impure anode case with refining)

(B) Cathode: Hydrogen gas; Anode: Oxygen gas

(C) Cathode:  $\text{Cu}^{2+}$  ions; Anode:  $\text{SO}_4^{2-}$  ions

(D) Cathode: Copper oxide; Anode: Sulfur dioxide

**Q37.** The solubility of calcium hydroxide in water decreases with increasing temperature (inverse temperature dependence). This indicates that the dissolution of  $\text{Ca}(\text{OH})_2$  is:

(A) Exothermic (dissolution releases heat, contradicting Le Chatelier's principle expectation)

(B) Endothermic (typical for salt dissolution)

(C) Entropy-driven (positive  $\Delta S$  dominates despite unfavorable enthalpy)

(D) Neither exothermic nor endothermic (purely kinetic effect)

**Q38.** In the bromination of aromatic compounds, the reactivity order is: phenol > aniline > benzene > nitrobenzene. This order reflects:

(A) The electron-donating ability of substituents (activating/deactivating effects)

(B) The size of substituent groups

(C) The electronegativity of substituent atoms

(D) The melting point differences of the products

**Q39.** The enzyme pepsin (a protease) has an optimal pH of 1.5-2.5 (stomach acid). At higher pH values, the activity of pepsin decreases dramatically due to:

(A) Denaturation of the enzyme protein structure at alkaline pH

(B) Protonation of amino acid residues at the active site required for catalysis



- (C) Inactivation of the substrate (protein) at higher pH
- (D) Loss of cofactors required for enzyme activity

**Q40.** In the preparation of biodegradable plastics, polylactic acid (PLA) is synthesized from lactic acid monomers through:

- (A) Condensation polymerization with elimination of water molecules forming ester linkages
- (B) Addition polymerization via free radical mechanism
- (C) Ring-opening polymerization of cyclic lactide intermediate
- (D) Ionic polymerization in the presence of Ziegler-Natta catalysts



**Detailed Solutions****Q1.****Solution****Concept:**

In esterification reactions using coupling reagents like DCC-DMAP, the mechanism does not involve carbocation intermediates or nucleophilic acyl substitution on the alcohol carbon. Instead, the reaction activates the carboxylic acid, and the nucleophilic attack occurs at the carboxyl carbon of the acid. The stereochemistry at the alcohol's chiral center is preserved because no bonds to the chiral center are broken or rearranged.

**Solution:**

- (a) The DCC-DMAP coupling mechanism activates the carboxylic acid by formation of an O-acylisourea intermediate.
- (b) The alcohol attacks the carbonyl carbon of the activated acid in a direct esterification process.
- (c) No bonds to the chiral carbon of the alcohol are cleaved; the C-O bond formation is to the original carbon that remains unchanged in stereochemistry.
- (d) The configuration of the (R)-stereocenter in the alcohol is completely retained throughout the reaction.
- (e) Therefore, the ester product retains the (R)-configuration at the alcohol-derived carbon.

**Final Answer:** (R)-configuration (retained)

**Answer:** (B)

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Q2.

**Solution****Concept:**

Equilibrium systems respond to changes in pressure according to Le Chatelier's Principle. For the dimerization equilibrium  $N_2O_4 \rightleftharpoons 2NO_2$ , the forward reaction increases the number of gas molecules (1 mol  $\rightarrow$  2 mol). Increasing pressure favors the side with fewer moles of gas, thus shifting the equilibrium to the left toward  $N_2O_4$ .

**Solution:**

- The equilibrium dissociation can be quantified by the degree of dissociation  $\alpha$ , which represents the fraction of  $N_2O_4$  that has decomposed.
- Isothermal compression increases the total pressure while maintaining constant temperature.
- According to Le Chatelier, the system shifts toward fewer moles of gas (the  $N_2O_4$  side).
- This shift to the left corresponds to a decrease in the degree of dissociation  $\alpha$  (less decomposition).
- The diagram shows that as pressure increases,  $\alpha$  decreases along the equilibrium curve.

**Final Answer:** Decrease

**Answer: (B)**

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Q3.

**Solution****Concept:**

The electronic configuration of Cu(II) is  $[Ar]3d^9$ , containing one unpaired d-electron. The term symbol for a single unpaired electron in a d orbital uses the ground state multiplicity  $2S + 1 = 2$  (doublet) and the total angular momentum. The blue color of  $[Cu(NH_3)_4]^{2+}$  arises from d-d transitions.

**Solution:**

- Copper(II) has the configuration  $[Ar]3d^9$  (one unpaired electron in the d orbitals).
- For a single unpaired electron,  $S = 1/2$ , giving a multiplicity of  $2S+1 = 2$  (doublet state).
- The  $d^9$  configuration corresponds to a  $^2D$  term symbol.
- For less than half-filled d orbitals, the ground state has  $J = |L - S| = |2 - 1/2| = 3/2$ .
- Therefore, the ground state term symbol is  $^2D_{3/2}$ .

**Final Answer:**  $d^9, ^2D_{3/2}$

**Answer: (C)**

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Q4.

**Solution****Concept:**

Persistent organic pollutants (POPs) are defined by their high persistence in the environment, which is determined by the strength of the chemical bonds in the molecule. DDT contains multiple C-Cl bonds, which are strong and difficult to cleave by hydrolysis, photolysis, or biodegradation.

**Solution:**

- (a) DDT (dichlorodiphenyltrichloroethane) has the structure with multiple aromatic rings substituted with chlorine atoms.
- (b) Each C-Cl bond has a bond dissociation energy around 340 kJ/mol, making it very resistant to cleavage.
- (c) The molecule lacks functional groups like hydroxyl (-OH) or ester groups that would be susceptible to hydrolytic degradation.
- (d) The strong C-Cl bonds prevent microbial degradation, photochemical degradation, and chemical hydrolysis.
- (e) This chemical stability leads to persistence in the environment and bioaccumulation in food chains.

**Final Answer:** Presence of multiple C-Cl bonds with high bond dissociation energy

**Answer: (B)**

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Q5.

**Solution****Concept:**

The SN2 mechanism requires the nucleophile to approach from the back side of the C-X bond at a 180° angle to displace the leaving group. Cyclopropane rings have inherent geometric constraints that prevent this anti-periplanar geometry.

**Solution:**

- (a) Cyclopropane is a three-membered ring with C-C-C angles of approximately 60° (compared to 109.5° in normal alkanes).
- (b) The three-membered ring structure creates severe steric crowding around the central carbon.
- (c) For an SN2 reaction, the nucleophile must approach from the rear side of the C-Br bond at a 180° angle.
- (d) The ring geometry prevents this back-side approach; the rear side is occupied by ring carbons and hydrogens.
- (e) Therefore, the ring-substituted carbocation cannot undergo normal SN2 displacement, making the reaction extremely slow.

**Final Answer:** Steric hindrance from the cyclopropane ring preventing back-side attack

**Answer:** (B)

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Q6.

**Solution****Concept:**

For an exothermic reaction (negative  $\Delta H$ ), increasing temperature shifts the equilibrium toward the reactants, decreasing the yield of products. To maximize yield in an exothermic reaction, conditions should favor the product side: decreasing temperature or increasing pressure (if the forward reaction reduces mole numbers).

**Solution:**

- (a) The reaction is exothermic with  $\Delta H = -20 \text{ kJ/mol}$  (energy is released).
- (b) Increasing temperature adds thermal energy, which shifts equilibrium toward the endothermic direction (backward, toward reactants).
- (c) Decreasing temperature removes thermal energy, shifting equilibrium forward (toward products) to counteract the change.
- (d) For the stoichiometry  $A(g) + B(g) \rightleftharpoons C(g)$ , the forward reaction decreases total moles of gas ( $2 \rightarrow 1$ ).
- (e) Either decreasing temperature OR increasing pressure would maximize product yield; decreasing temperature is the most effective for exothermic reactions.

**Final Answer:** Decrease temperature

**Answer: (B)**

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Q7.

**Solution****Concept:**

The crystal field splitting parameter ( $\Delta_o$ ) is determined by the strength of the ligand field. Different ligands create different magnitudes of splitting. Chloride is a weaker field ligand than water, so replacing water with chloride will decrease  $\Delta_o$ .

**Solution:**

- (a) Water is a moderate-field ligand (intermediate in the spectrochemical series).
- (b) Chloride is a weak-field ligand (lower in the spectrochemical series than water).
- (c) The spectrochemical series ranks ligands by their ability to cause d-orbital splitting:  
 $I^- < Br^- < Cl^- < NO_3^- < H_2O < NH_3 < en < NO_2^- < CN^-$ .
- (d) Replacing a water molecule with a weaker chloride ligand results in a smaller overall crystal field splitting.
- (e) Therefore,  $\Delta_o$  decreases when water is replaced by chloride.

**Final Answer:** Decrease ( $Cl^-$  is a weaker field ligand than  $H_2O$ )

**Answer: (B)**

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Q8.

**Solution****Concept:**

In saponification (alkaline ester hydrolysis), the carboxylate anion formed is resonance-stabilized by the two equivalent C-O double bond canonical forms. This resonance stabilization makes the carboxylate anion highly stable and prevents re-esterification, making the overall reaction essentially irreversible.

**Solution:**

- (a) The saponification reaction:  $R - COO - R' + NaOH \rightarrow R - COO^- Na^+ + R' - OH$ .
- (b) The product carboxylate ion ( $R - COO^-$ ) is stabilized by resonance over two equivalent structures.
- (c) This resonance stabilization makes the carboxylate anion very stable and resistant to nucleophilic attack by alkoxide.
- (d) The backward reaction (re-esterification) would require the carboxylate anion to accept the alkoxide as a leaving group, which is energetically unfavorable.
- (e) Therefore, saponification is essentially irreversible under normal conditions.

**Final Answer:** The carboxylate anion formed is stabilized by resonance and does not re-esterify easily

**Answer:** (A)

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Q9.

**Solution****Concept:**

The enthalpy of vaporization ( $\Delta H_{vap}$ ) represents the energy required to convert a liquid to a gas. As temperature increases, the internal kinetic energy of molecules increases, requiring less additional energy to overcome intermolecular forces. Therefore,  $\Delta H_{vap}$  decreases with increasing temperature, approaching zero at the critical point.

**Solution:**

- (a) At lower temperatures, molecules have lower kinetic energy and require more energy to escape from the liquid phase.
- (b) As temperature increases, molecular kinetic energy increases, reducing the energy barrier for vaporization.
- (c) The Clausius-Clapeyron equation, though commonly written as a linear relationship, shows that  $\Delta H_{vap}$  is temperature-dependent.
- (d) Experimentally,  $\Delta H_{vap}$  decreases as temperature approaches the critical temperature (where  $\Delta H_{vap}$  approaches zero).
- (e) The diagram shows this inverse relationship: as T increases,  $\Delta H_{vap}$  decreases.

**Final Answer:** Decrease

**Answer:** (B)

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Q10.

**Solution****Concept:**

Acid-catalyzed hydration of alkenes proceeds through a carbocation intermediate, which can rearrange via hydride or alkyl shifts to form a more stable carbocation. This carbocation rearrangement leads to skeletal rearrangement of the carbon skeleton. Oxymercuration, followed by reduction, bypasses the free carbocation intermediate by using a mercurinium ion intermediate, preventing rearrangement.

**Solution:**

- (a) In acid-catalyzed hydration,  $H^+$  adds to the alkene, forming a carbocation intermediate.
- (b) This carbocation can undergo rearrangement (1,2-hydride shift or 1,2-alkyl shift) to form a more stable carbocation.
- (c) The rearranged carbocation leads to a different product than expected from simple Markovnikov addition.
- (d) In oxymercuration ( $Hg(OAc)_2$  followed by  $NaBH_4$  reduction), a mercurinium ion intermediate forms instead of a carbocation.
- (e) The mercurinium ion is a tight, symmetrical intermediate that does not rearrange, preserving the original carbon skeleton.

**Final Answer:** Acid-catalyzed hydration can produce rearranged products via carbocation shifts, while oxymercuration prevents rearrangement

**Answer: (B)**

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Q11.

**Solution****Concept:**

Vulcanization of rubber involves the formation of covalent cross-links between polymer chains. Sulfur atoms form bridges between adjacent chains, creating disulfide (C-S-S-C) and monosulfide (C-S-C) cross-links. These covalent cross-links dramatically improve the mechanical properties of the rubber.

**Solution:**

- (a) Natural rubber (cis-polyisoprene) has double bonds in the backbone chain.
- (b) Sulfur atoms react with these double bonds, adding across the alkene to form cross-links.
- (c) The cross-links formed are primarily disulfide bridges (C-S-S-C) and monosulfide linkages (C-S-C).
- (d) These covalent bonds between chains increase rigidity, tensile strength, and elasticity of the rubber.
- (e) Hydrogen bonds cannot form between hydrocarbon chains; ionic and peptide bonds are not relevant to rubber chemistry.

**Final Answer:** Disulfide bonds (C-S-S-C and C-S-C cross-links)

**Answer:** (C)

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Q12.

**Solution****Concept:**

In the Gabriel synthesis, phthalamide is deprotonated to form a stabilized carbanion nucleophile. The carbanion attacks an alkyl halide to form an N-alkyl phthalamide. Over-alkylation does not occur because after the first nucleophilic displacement, the product (N-alkyl phthalamide) is not a strong nucleophile like the starting phthalamide anion.

**Solution:**

- (a) Phthalamide (from phthalic anhydride) has two electron-withdrawing carbonyl groups that stabilize the negative charge on nitrogen.
- (b) The phthalamide anion (N-carbanion) is a strong nucleophile due to resonance stabilization by the two nearby carbonyl groups.
- (c) After the first  $S_N2$  displacement with an alkyl halide, the product is N-alkyl phthalamide.
- (d) The N-alkyl product is no longer anionic and has lost the nucleophilic character; it cannot easily undergo further displacement.
- (e) Therefore, the reaction stops after one alkylation, preventing over-alkylation and ensuring formation of primary amines.

**Final Answer:** The phthalamide anion is stabilized by two carbonyl groups, making it a poor nucleophile for secondary attack

**Answer:** (A)

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Q13.

**Solution****Concept:**

The Tyndall effect is the scattering of light by colloidal particles. Colloids have particle sizes between 1-1000 nm, which is large enough to scatter visible light significantly (but not so large that they sediment like suspensions). True solutions with molecules smaller than 1 nm do not show the Tyndall effect because they do not scatter light noticeably.

**Solution:**

- (a) Colloidal particles (1-1000 nm) are large enough to interact with visible light wavelengths (400-700 nm).
- (b) When light passes through a colloidal dispersion, particles scatter the light in all directions due to diffraction and reflection.
- (c) This scattered light makes the path of a light beam visible when viewed from the side (Tyndall beam).
- (d) True solutions have particle sizes below 1 nm (molecules or ions) and do not scatter light significantly.
- (e) Suspensions have particle sizes above 1000 nm and undergo sedimentation rather than maintaining colloidal stability.

**Final Answer:** Scattering of light by colloidal particles (size 1-1000 nm) which is intermediate between solution and suspension

**Answer: (A)**

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Q14.

**Solution****Concept:**

Half-filled orbital configurations ( $p^3$ ,  $d^5$ , etc.) have special stability due to exchange energy. Electrons in half-filled orbitals occupy separate spatial regions with parallel spins, maximizing exchange energy. Phosphorus with a  $p^3$  configuration shows higher ionization energy than the sulfur ( $p^4$ ), contradicting the normal periodic trend.

**Solution:**

- (a) The electronic configuration of phosphorus is  $[\text{Ne}]3s^23p^3$  (three unpaired electrons in p orbitals).
- (b) The  $p^3$  configuration represents a half-filled p subshell with one electron in each of the three p orbitals.
- (c) Half-filled configurations are particularly stable due to maximum exchange energy (electrons with parallel spins in separate orbitals).
- (d) Sulfur has  $[\text{Ne}]3s^23p^4$  (one paired and two unpaired electrons), which lacks this exchange stabilization.
- (e) Therefore, phosphorus has higher ionization energy than sulfur, contrary to the normal trend of decreasing ionization energy across a period.

**Final Answer:** The half-filled  $p^3$  orbital configuration of P is particularly stable

**Answer:** (A)

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Q15.

**Solution****Concept:**

Kinetic control describes a situation where the product distribution is determined by reaction rates (activation energies) rather than thermodynamic stability. The kinetic product is formed faster due to a lower activation energy, while the thermodynamic product is more stable but forms more slowly.

**Solution:**

- (a) In the 1,2-addition vs. 1,4-addition of HBr to a conjugated diene, two possible products can form.
- (b) At low temperatures, the 1,2-addition product forms faster (lower activation energy) and dominates, even though it may not be the most stable.
- (c) At higher temperatures, the reaction system has enough energy to interconvert between kinetic and thermodynamic products.
- (d) The kinetic product is the major product at low temperature due to its lower activation energy barrier.
- (e) This is a classic example of kinetic control: the reaction is stopped before equilibrium is reached, trapping the kinetic product.

**Final Answer:** Formation of 1,2-addition product at low temperature in a diene reaction (kinetic product dominates)

**Answer: (B)**

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Q16.

**Solution****Concept:**

The solubility product expression for  $Mg(OH)_2$  is  $K_{sp} = [Mg^{2+}][OH^-]^2$ . Given the pH, we can calculate the  $[OH^-]$  concentration, and then use  $K_{sp}$  to find the molar solubility of magnesium ions.

**Solution:**

- (a) Given pH = 10.5, we calculate pOH = 14 - 10.5 = 3.5.
- (b) Therefore,  $[OH^-] = 10^{-3.5} = 3.16 \times 10^{-4}$  M.
- (c) The solubility product expression is:  $K_{sp} = [Mg^{2+}][OH^-]^2 = 1.8 \times 10^{-11}$ .
- (d) Solving for the molar solubility:  $[Mg^{2+}] = \frac{K_{sp}}{[OH^-]^2} = \frac{1.8 \times 10^{-11}}{(3.16 \times 10^{-4})^2}$ .
- (e) Calculating:  $[Mg^{2+}] = \frac{1.8 \times 10^{-11}}{10 \times 10^{-8}} = 1.8 \times 10^{-4}$  M  $1.4 \times 10^{-4}$  M.

**Final Answer:**  $1.4 \times 10^{-4}$  M

**Answer: (A)**

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Q17.

**Solution****Concept:**

The Jahn-Teller effect states that non-linear molecules with degenerate electronic states undergo distortion to remove the degeneracy and lower the overall energy. Cu(II) with a  $d^9$  configuration has a partially filled d subshell with degeneracy that is relieved by distortion.

**Solution:**

- (a) Cu(II) has the electron configuration  $[\text{Ar}]3d^9$  (one d-electron hole).
- (b) In a regular tetrahedral or octahedral field, the d orbitals are degenerate or partially degenerate.
- (c) The  $d^9$  system has degeneracy in the d-orbital manifold (e.g., in an octahedral field, the  $d_{z^2}$  and  $d_{x^2-y^2}$  orbitals are degenerate).
- (d) The Jahn-Teller theorem states that degenerate electronic states are unstable and the molecule distorts to relieve degeneracy.
- (e) For  $[\text{CuCl}_4]^{2-}$ , tetrahedral geometry distorts to square planar to separate the degenerate d-orbital energies and lower the system's total energy.

**Final Answer:** The  $d^9$  configuration of Cu(II) undergoes Jahn-Teller distortion to relieve electronic strain

**Answer: (A)**

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Q18.

**Solution****Concept:**

Ozonolysis of alkenes involves 1,3-dipolar cycloaddition of ozone (a 1,3-dipole) to the C=C double bond (a dipolarophile) to form a primary ozonide. The primary ozonide is unstable and rearranges via a retro-cycloaddition and recombination to form a more stable secondary ozonide.

**Solution:**

- (a) Ozone ( $O_3$ ) acts as a 1,3-dipole with oxygen atoms at the terminal positions (1,3-positions) and the central oxygen.
- (b) The alkene acts as a dipolarophile, and the [3+2] cycloaddition forms a cyclic primary ozonide.
- (c) The primary ozonide (1,2,4-trioxolane) is unstable because the O-O bond is weak and strained.
- (d) The primary ozonide undergoes a retro-cycloaddition, breaking the O-O bond and releasing a zwitterionic intermediate.
- (e) The zwitterion recombines via a [3+2] cycloaddition in a different orientation to form the more stable secondary ozonide.

**Final Answer:** A 1,3-dipolar cycloaddition followed by a retro-cycloaddition and recombination

**Answer: (A)**

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Q19.

**Solution****Concept:**

Gay-Lussac's Law (a special case of the ideal gas law) states that at constant volume, the pressure of a gas is directly proportional to its absolute temperature:  $P_1/T_1 = P_2/T_2$ .

**Solution:**

- (a) Gay-Lussac's Law applies to gases at constant volume and constant amount of substance.
- (b) The relationship is:  $P/T = \text{constant}$ , or  $P_1/T_1 = P_2/T_2$ .
- (c) Initial temperature:  $T_1 = 273 \text{ K}$ ; Final temperature:  $T_2 = 546 \text{ K} = 2 \times T_1$ .
- (d) Therefore:  $P_2 = P_1 \times (T_2/T_1) = P_1 \times (546/273) = P_1 \times 2$ .
- (e) The pressure doubles when the absolute temperature doubles at constant volume.

**Final Answer:** Double (Gay-Lussac's Law:  $P_1/T_1 = P_2/T_2$ )

**Answer: (A)**

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Q20.

**Solution****Concept:**

Carbonic acid is a weak acid that exists in equilibrium with dissolved  $\text{CO}_2$  and water. The dissociation is progressive:  $\text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$  ( $K_{a1} = 4.3 \times 10^{-7}$ ), and  $\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}$  ( $K_{a2} = 4.7 \times 10^{-11}$ ). At pH 7, the  $\text{HCO}_3^-$  species is the predominant form.

**Solution:**

- (a) The  $K_{a1}$  for carbonic acid is approximately  $4.3 \times 10^{-7}$  ( $\text{p}K_{a1} = 6.4$ ).
- (b) The  $K_{a2}$  for the bicarbonate ion is approximately  $4.7 \times 10^{-11}$  ( $\text{p}K_{a2} = 10.3$ ).
- (c) At pH 7, which is between  $\text{p}K_{a1}$  (6.4) and  $\text{p}K_{a2}$  (10.3), the intermediate species  $\text{HCO}_3^-$  is predominant.
- (d) At  $\text{pH} < \text{p}K_{a1}$ ,  $\text{H}_2\text{CO}_3$  dominates; at  $\text{pH} > \text{p}K_{a2}$ ,  $\text{CO}_3^{2-}$  dominates.
- (e) Since pH 7 falls between the two  $\text{p}K_a$  values, bicarbonate ion ( $\text{HCO}_3^-$ ) is the primary species.

**Final Answer:**  $\text{HCO}_3^-$  (bicarbonate ion)

**Answer: (B)**

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Q21.

**Solution****Concept:**

The cumene process (also known as the isopropylbenzene process) converts benzene to phenol through several steps: (1) Friedel-Crafts alkylation to form cumene, (2) oxidation to cumene hydroperoxide, (3) acid-catalyzed rearrangement to phenol and acetone. The co-production of acetone is economically valuable, making this route industrially preferred despite requiring more steps than direct hydroxylation.

**Solution:**

- (a) The cumene process starts with Friedel-Crafts alkylation of benzene with propylene to form cumene (isopropylbenzene).
- (b) Cumene is oxidized with air/oxygen to form cumene hydroperoxide.
- (c) Acid catalysis (typically  $\text{H}_2\text{SO}_4$ ) causes the Criegee rearrangement: the hydroperoxide rearranges to form phenol and acetone.
- (d) The acetone co-product has significant commercial value (used in solvents, production of other chemicals).
- (e) This economic advantage of co-producing valuable acetone makes the multi-step cumene process more profitable than direct hydroxylation, despite additional complexity.

**Final Answer:** The co-product acetone has significant commercial value

**Answer: (B)**

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Q22.

**Solution****Concept:**

The dipole moment is the vector sum of individual bond dipoles. In water, each O-H bond is polar (O is more electronegative than H), creating bond dipoles pointing from H toward O. However, the bent molecular geometry of water ( $104.5^\circ$  bond angle) causes partial cancellation of these bond dipoles.

**Solution:**

- (a) Each O-H bond in water is polar due to electronegativity difference: O (3.44) > H (2.20).
- (b) Each O-H bond dipole points from H toward O (the more negative end).
- (c) If water were linear, the two O-H dipoles would point in opposite directions and cancel completely.
- (d) Because water has a bent geometry ( $104.5^\circ$  angle), the two O-H bond dipoles do not completely cancel.
- (e) The vector sum of the two bond dipoles results in a net dipole moment of 1.85 D, which is less than the sum of the individual bond dipoles (2.4 D).
- (f) This partial cancellation demonstrates how molecular geometry affects the net dipole moment.

**Final Answer:** Partial cancellation of individual bond dipoles due to the bent molecular geometry

**Answer: (B)**

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Q23.

**Solution****Concept:**

The Lineweaver-Burk plot is derived from the Michaelis-Menten equation by taking the reciprocal of both sides:  $1/v_0 = (K_m/V_{max})(1/[S]) + 1/V_{max}$ . This is a linear equation of the form  $y = mx + b$ , where the slope and intercepts provide kinetic parameters.

**Solution:**

- (a) The Michaelis-Menten equation is:  $v_0 = \frac{V_{max}[S]}{K_m + [S]}$ .
- (b) Taking reciprocals:  $\frac{1}{v_0} = \frac{K_m + [S]}{V_{max}[S]} = \frac{K_m}{V_{max}[S]} + \frac{1}{V_{max}}$ .
- (c) Rearranging:  $\frac{1}{v_0} = \frac{K_m}{V_{max}} \left( \frac{1}{[S]} \right) + \frac{1}{V_{max}}$ .
- (d) In the linear form  $y = mx + b$ : the y-intercept =  $1/V_{max}$ , the slope =  $K_m/V_{max}$ , and the x-intercept =  $-1/K_m$ .
- (e) From these parameters,  $V_{max}$  and  $K_m$  (the Michaelis constant, representing substrate concentration at half maximal velocity) can be determined.

**Final Answer:** y-intercept =  $1/V_{max}$  and x-intercept =  $-1/K_m$

**Answer: (A)**

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Q24.

**Solution****Concept:**

The synthesis of urea from ammonia and carbon dioxide occurs in two main steps. First, ammonia and  $\text{CO}_2$  combine to form ammonium carbamate ( $\text{NH}_2\text{COONH}_4$ ), which is an unstable intermediate. Under further heating and dehydration, carbamate converts to urea ( $\text{NH}_2\text{CONH}_2$ ) with the loss of two water molecules or one ammonia molecule.

**Solution:**

- (a) The reaction of ammonia with carbon dioxide:  $2\text{NH}_3 + \text{CO}_2 \rightarrow \text{NH}_2\text{COONH}_4$  (ammonium carbamate forms as an intermediate).
- (b) Ammonium carbamate is unstable and decomposes under heating:  $\text{NH}_2\text{COONH}_4 \rightarrow \text{NH}_2\text{CONH}_2 + \text{H}_2\text{O}$  (urea is formed).
- (c) The overall process is:  $2\text{NH}_3 + \text{CO}_2 \rightarrow \text{NH}_2\text{CONH}_2 + \text{H}_2\text{O}$  (net reaction showing urea formation).
- (d) The synthesis is conducted at high temperature (around  $150\text{-}200^\circ\text{C}$ ) and high pressure (100-200 atm) to favor the formation of urea.
- (e) The Haber-Bosch process separately produces ammonia from  $\text{N}_2$  and  $\text{H}_2$ ; this urea synthesis uses the ammonia produced by Haber-Bosch.

**Final Answer:**  $2\text{NH}_3 + \text{CO}_2 \rightarrow \text{NH}_2\text{COONH}_4$  (ammonium carbamate, intermediate)

**Answer:** (A)

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Q25.

**Solution****Concept:**

The Hofmann elimination reaction converts quaternary ammonium salts ( $R_4N^+X^-$ ) into alkenes. The reaction proceeds by an E2 mechanism with anti-periplanar geometry. A key feature of Hofmann elimination is that it produces the least-substituted (terminal) alkene, opposite to Zaitsev's rule, which predicts the more-substituted alkene.

**Solution:**

- (a) The Hofmann elimination uses a quaternary ammonium salt ( $R_4N^+ Cl^-$ ) and strong base (typically NaOH or KOH, sometimes heated).
- (b) The reaction proceeds by an E2 mechanism requiring anti-periplanar geometry (H and leaving group  $N(CH_3)_3$  on opposite sides).
- (c) Unlike Zaitsev's rule (which gives the more-substituted alkene), Hofmann elimination favors the less-substituted (terminal) alkene.
- (d) This is because the bulky trimethylammonium leaving group  $N(CH_3)_3^+$  creates steric hindrance, directing the base to abstract a less sterically hindered hydrogen.
- (e) Therefore, Hofmann elimination produces the Hofmann product (minor alkene, least substituted).

**Final Answer:** The minor alkene product (least substituted alkene, Hofmann product)

**Answer: (B)**

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Q26.

**Solution****Concept:**

Activated carbon's high adsorption capacity derives from its extensive internal pore structure. The material contains a network of micropores (< 2 nm) and mesopores (2-50 nm) that dramatically increase the surface area available for adsorption. This internal porosity, created during the activation process, allows adsorbates to penetrate deep into the material.

**Solution:**

- (a) Activated carbon is produced from carbonaceous materials (coal, coconut shells, wood) through partial oxidation and removal of non-carbon elements.
- (b) The activation process (steam or CO<sub>2</sub> activation at high temperature) creates an extensive internal pore network.
- (c) Micropores (diameters < 2 nm) and mesopores (2-50 nm) create an enormous internal surface area.
- (d) The surface area of activated carbon can reach 3000 m<sup>2</sup>/g, compared to only a few m<sup>2</sup>/g for non-activated carbon.
- (e) This high surface area is what enables activated carbon to adsorb large quantities of pollutants like organic contaminants and chlorine from water.

**Final Answer:** Creating a microporous and mesoporous internal structure

**Answer:** (A)

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Q27.

**Solution****Concept:**

Spontaneous redox reactions are determined by comparing reduction potentials. The species with the higher (more positive) reduction potential is reduced (gains electrons), while the species with the lower reduction potential is oxidized (loses electrons). The half-reaction with the higher  $E^\circ$  is the cathode (reduction), and the lower  $E^\circ$  is the anode (oxidation).

**Solution:**

- (a) Given:  $Fe^{3+}/Fe^{2+}$  has  $E = +0.77$  V (higher, more oxidizing).
- (b) Given:  $I_2/I^-$  has  $E = +0.54$  V (lower, less oxidizing).
- (c) The species with higher  $E^\circ$  ( $Fe^{3+}$ ) will be reduced:  $Fe^{3+} + e^- \rightarrow Fe^{2+}$ .
- (d) The species with lower  $E^\circ$  ( $I_2$ ) will be oxidized (reversed):  $2I^- \rightarrow I_2 + 2e^-$ .
- (e) However, the actual reaction involves  $Fe^{3+}$  oxidizing  $I^-$ :  $2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$ .
- (f) This spontaneous reaction produces  $Fe^{2+}$  and  $I_2$ .

**Final Answer:**  $Fe^{2+}$  and  $I_2$  ( $Fe^{3+}$  oxidizes  $I^-$  to  $I_2$ )

**Answer: (A)**

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Q28.

**Solution****Concept:**

In IUPAC nomenclature of alkynes, the triple bond position determines the numbering of the carbon chain. The triple bond receives priority in the numbering scheme (like double bonds), and the principal chain is chosen to include the triple bond with the lowest numbers.

**Solution:**

- (a) The compound is:  $\text{HC}\equiv\text{C}-\text{CH}_2-\text{CH}(\text{CH}_3)_2$ .
- (b) Identify the functional group: a triple bond (alkyne) between carbons 1 and 2.
- (c) Main chain includes the triple bond at positions 1-2, followed by  $\text{CH}_2$  at position 3, and  $\text{CH}$  at position 4.
- (d) At position 4, the  $\text{CH}$  is bonded to two methyl groups, creating a total of 5 carbons in the longest chain.
- (e) The IUPAC name is: 4-methylpent-1-yne (5-carbon chain with alkyne at position 1 and a methyl substituent at position 4).

**Final Answer:** 4-methylpent-1-yne

**Answer:** (C)

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Q29.

**Solution****Concept:**

In the Born-Haber cycle, the lattice enthalpy represents the energy required to completely separate one mole of an ionic solid into its gaseous ions. This is typically the most energetically demanding step in the cycle because it requires breaking apart the entire crystal structure with all of its electrostatic interactions.

**Solution:**

- (a) The Born-Haber cycle includes steps like: (1) Sublimation of metal:  $M(s) \rightarrow M(g)$  - moderate energy (2) Ionization of metal:  $M(g) \rightarrow M^{n+}(g) + ne^{-}$  - high energy (ionization energy) (3) Dissociation of non-metal:  $X_2(g) \rightarrow 2X(g)$  - moderate energy (4) Electron affinity of non-metal:  $X(g) + e^{-} \rightarrow X^{-}(g)$  - usually exothermic (5) Lattice enthalpy:  $M^{n+}(g) + nX^{-}(g) \rightarrow MX_n(s)$  - very large energy release
- (b) Lattice enthalpy is the reverse of the process of completely separating the crystal, which requires breaking thousands of electrostatic interactions simultaneously.
- (c) Ionization energy is significant but typically less than lattice enthalpy for most compounds.
- (d) Sublimation energy is generally smaller than ionization energy.

**Final Answer:** Lattice enthalpy of the ionic crystal (breaking apart the solid)

**Answer: (B)**

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Q30.

**Solution****Concept:**

The electronic absorption bands in complex ions arise from transitions between electronic energy levels. Platinum(II) complexes can exhibit metal-to-ligand charge transfer (MLCT), where an electron from a filled d orbital on the metal is excited to an empty orbital on the ligand. This is typically a stronger absorption than d-d transitions.

**Solution:**

- (a) Platinum(II) has the electron configuration  $[\text{Xe}]4f^{14}5d^8$ , with filled d orbitals.
- (b) Chloride is a good  $\pi$ -donor ligand and can accept electron density in  $\pi^*$  or  $\sigma^*$  orbitals.
- (c) Metal-to-ligand charge transfer (MLCT) transitions involve promotion of an electron from a filled d orbital on Pt to an empty orbital on Cl (such as antibonding orbitals).
- (d) MLCT transitions typically occur at lower energies (longer wavelengths) than d-d transitions within the d manifold.
- (e) The strong absorption bands observed in  $[\text{PtCl}_4]^{2-}$  are primarily due to MLCT transitions.
- (f) Ligand-to-metal charge transfer (LMCT) would involve electron promotion from the ligand to empty d orbitals on Pt, which is less favorable given that Pt(II) is already electron-rich.

**Final Answer:** Metal-to-ligand charge transfer (MLCT) transitions

**Answer:** (A)

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Q31.

**Solution****Concept:**

The reducing capability of complex metal hydrides depends on the nucleophilicity of the transferred hydride. Aluminum (*Al*) is less electronegative than boron (*B*), making the *Al* – *H* bond more polarized than the *B* – *H* bond. This polar nature allows  $\text{LiAlH}_4$  to release hydride ions more readily to attack challenging electrophiles like carboxylic acids.

**Solution:**

- (a) Carboxylic acids are resistant to weak nucleophilic attacks because the acidic proton deprotonates the hydride reagent initially, forming a resonance-stabilized carboxylate anion that repels further nucleophilic attack.
- (b) The highly polar *Al* – *H* bond in  $\text{LiAlH}_4$  gives the hydride high kinetic reactivity, allowing it to overcome this electronic repulsion and reduce the carbonyl group.
- (c) Conversely, the *B* – *H* bond in  $\text{NaBH}_4$  is more covalent and stable, making it a milder reducing agent that can only reduce more electrophilic functional groups like aldehydes and ketones.
- (d) Sodium and lithium counter-ions provide coordination assistance, but the core reactivity difference lies fundamentally in the polarization of the metal-hydrogen bonds.

**Final Answer:** The Al-H bond in  $\text{LiAlH}_4$  is more polar and delivers hydride more effectively than the B-H bond in  $\text{NaBH}_4$

**Answer:** (A)

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Q32.

**Solution****Concept:**

Valence Shell Electron Pair Repulsion (VSEPR) theory determines molecular geometry by minimizing electrostatic repulsion between electron pairs around a central atom. For the xenon pentafluoride cation ( $\text{XeF}_5^+$ ), calculating the steric number provides the distribution of bonding pairs and lone pairs.

**Solution:**

- Xenon ( $\text{Xe}$ ) has 8 valence electrons. The positive charge removes 1 electron, leaving 7. The five fluorine atoms share 5 electrons, giving 12 total electrons around xenon.
- These 12 electrons form 6 electron pairs, indicating an octahedral steric arrangement (steric number = 6).
- Out of these 6 pairs, 5 are bonding pairs ( $\sigma$ -bonds to fluorine) and 1 is a lone pair.
- An octahedral arrangement with one lone pair projects a square pyramidal molecular geometry, with the lone pair occupying an axial position to maximize space.

**Final Answer:** Square pyramidal

**Answer:** (A)

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Q33.

**Solution****Concept:**

Crystal Field Theory (CFT) explains the electronic behavior and magnetic properties of transition metal complexes. Ligands split the degenerate  $d$ -orbitals of a metal into  $t_{2g}$  and  $e_g$  subsets. The magnitude of this splitting energy ( $\Delta_o$ ) determines whether electrons pair up or occupy higher energy states.

**Solution:**

- In the complex  $[\text{Fe}(\text{CN})_6]^{4-}$ , iron is in the +2 oxidation state ( $\text{Fe}^{2+}$ ), giving it a  $d^6$  electronic configuration.
- Cyanide ( $\text{CN}^-$ ) is classified as a strong-field ligand at the high end of the spectrochemical series. It causes a substantial crystal field splitting energy ( $\Delta_o$ ).
- Because  $\Delta_o$  is larger than the spin-pairing energy, all six  $d$ -electrons pair up in the lower-energy  $t_{2g}$  orbitals ( $t_{2g}^6 e_g^0$ ).
- The total pairing of electrons results in a low-spin configuration that exhibits diamagnetic behavior due to the absence of unpaired electrons.

**Final Answer:** A strong field ligand causing large crystal field splitting, resulting in a low-spin (diamagnetic) complex

**Answer: (A)**

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Q34.

**Solution****Concept:**

The total greenhouse effect of an atmospheric gas depends on both its intrinsic Global Warming Potential (GWP) and its absolute atmospheric abundance. While gases like methane and nitrous oxide possess much higher GWPs molecule-for-molecule, their absolute trace quantities limit their total radiative forcing impact compared to more abundant gases.

**Solution:**

- (a) Carbon dioxide ( $\text{CO}_2$ ) is released in massive anthropogenic quantities through fossil fuel combustion and industrial processes, making its atmospheric concentration drastically higher than other synthetic greenhouse gases.
- (b) Additionally,  $\text{CO}_2$  lacks a rapid chemical sink in the atmosphere, leading to a long residence time that spans centuries.
- (c) Methane ( $\text{CH}_4$ ) has a higher short-term radiative warming efficiency but breaks down relatively quickly via hydroxyl radical oxidation within decades.
- (d) Therefore, the massive volume and cumulative atmospheric persistence of  $\text{CO}_2$  make it the dominant driver of anthropogenic climate change.

**Final Answer:** Carbon dioxide ( $\text{CO}_2$ ) due to high atmospheric concentration and long residence time

**Answer: (A)**

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Q35.

**Solution****Concept:**

The Michaelis constant ( $K_m$ ) is a foundational parameters in enzyme kinetics derived from the Michaelis-Menten model. It mathematically describes the relationship between the initial reaction velocity ( $v_0$ ) and the substrate concentration ( $[S]$ ).

**Solution:**

- (a) The Michaelis-Menten rate law is expressed as:  $v_0 = \frac{V_{\max}[S]}{K_m + [S]}$ .
- (b) Setting the initial velocity to exactly half of the theoretical maximum,  $v_0 = \frac{V_{\max}}{2}$ , allows the algebraic simplification of the rate equation.
- (c) Substituting this value yields  $\frac{V_{\max}}{2} = \frac{V_{\max}[S]}{K_m + [S]}$ , which simplifies directly to  $K_m + [S] = 2[S]$ , or  $K_m = [S]$ .
- (d) Thus,  $K_m$  is operationally defined as the exact substrate concentration required for the enzyme to function at half of its maximum velocity.

**Final Answer:** The substrate concentration at which the reaction rate is half of  $V_{\max}$

**Answer: (A)**

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Q36.

**Solution****Concept:**

Electrolysis with active electrodes involves competitive redox reactions governed by standard reduction potentials and electrode chemistry. When using copper electrodes in a copper sulfate solution ( $\text{CuSO}_4$ ), the copper metal substrate itself participates actively in the electrochemical processes.

**Solution:**

- (a) At the cathode, reduction takes place.  $\text{Cu}^{2+}$  ions from the solution possess a higher reduction potential than water molecules, meaning they are preferentially reduced to form metallic copper deposit:  $\text{Cu}^{2+} + 2\text{e}^- \longrightarrow \text{Cu}$ .
- (b) At the anode, oxidation takes place. Because copper is an active metal, the oxidation of the copper anode substrate ( $\text{Cu} \longrightarrow \text{Cu}^{2+} + 2\text{e}^-$ ) requires less energy than the oxidation of water or sulfate ions.
- (c) Consequently, the copper anode slowly dissolves into the solution to replenish the cations. This specific pair of reactions forms the basis of industrial electrorefining.

**Final Answer:** Cathode: Cu metal; Anode: Oxygen gas (pure copper anode case) or Cu metal dissolution (impure anode case with refining)

**Answer: (A)**

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Q37.

**Solution****Concept:**

The effect of temperature on chemical solubility equilibria is governed by Le Chatelier's principle. This principle states that a system at equilibrium will shift its position to counteract any external thermal stress applied to it.

**Solution:**

- (a) The dissolution equilibrium can be written as:  $\text{Ca(OH)}_2(\text{s}) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + 2 \text{OH}^{-}(\text{aq})$ .
- (b) When temperature is increased, the system shifts in the direction that absorbs heat to reduce thermal stress, favoring the endothermic pathway.
- (c) Because the solubility of  $\text{Ca(OH)}_2$  decreases with rising temperatures, the equilibrium shifts backward toward the solid reactant, meaning the reverse precipitation process absorbs heat.
- (d) It follows that the forward dissolution step must release heat into the surroundings, classifying it definitively as an exothermic process ( $\Delta H < 0$ ).

**Final Answer:** Exothermic (dissolution releases heat, contradicting Le Chatelier's principle expectation)

**Answer: (A)**

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Q38.

**Solution****Concept:**

Electrophilic aromatic substitution ( $S_EAr$ ) mechanisms proceed through the attack of an aromatic  $\pi$ -system on an electron-deficient electrophile. The rate-determining step involves the formation of a positively charged  $\sigma$ -complex (arenium ion), whose stability governs the overall reaction rate.

**Solution:**

- (a) Substituent groups bonded to the benzene ring alter its electron density through inductive and resonance mechanisms.
- (b) Hydroxyl ( $-OH$ ) and amino ( $-NH_2$ ) groups donate electron density into the ring through resonance stabilization, activating it toward electrophilic attack.
- (c) Phenol shows high reactivity because oxygen can stabilize the intermediate effectively, while aniline is highly active but slightly tempered relative to phenol depending on conditions.
- (d) Conversely, the nitro group ( $-NO_2$ ) strongly withdraws electron density, deactivating the ring and slowing down the reaction compared to unsubstituted benzene.

**Final Answer:** The electron-donating ability of substituents (activating/deactivating effects)

**Answer: (A)**

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Q39.

**Solution****Concept:**

Enzymes are highly specialized protein catalysts whose structural stability and catalytic activity depend strongly on the ionization states of their component amino acids. Changes in ambient  $pH$  disrupt the delicate electrostatic interactions that maintain their tertiary structure and active site configuration.

**Solution:**

- (a) Pepsin operates natively in highly acidic gastric fluid ( $pH$  1.5 – 2.5). Its active site depends on specific protonated amino acid residues to hold its catalytic form and bind substrates.
- (b) As  $pH$  rises toward neutral or alkaline levels, these essential proton donors lose their hydrogen ions to the basic medium.
- (c) This deprotonation breaks salt bridges and hydrogen bonds, causing the enzyme's three-dimensional polypeptide architecture to unravel.
- (d) This structural denaturation completely deforms the active site, destroying its catalytic capabilities permanently.

**Final Answer:** Denaturation of the enzyme protein structure at alkaline pH

**Answer:** (A)

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Q40.

**Solution****Concept:**

Poly(lactic acid) (PLA) can be generated by direct condensation of lactic acid, but achieving high molecular weight industrial-grade polymer requires a more controlled synthetic pathway to avoid thermodynamic limitations.

**Solution:**

- (a) Direct condensation polymerization of lactic acid removes water molecules, but this equilibrium process limits the chain length due to back-reactions with water.
- (b) To overcome this, lactic acid is first oligomerized and catalytically converted into a stable, cyclic dimer intermediate known as lactide.
- (c) This purified cyclic lactide undergoes Ring-Opening Polymerization (ROP) driven by the relief of ring strain.
- (d) ROP avoids the production of volatile secondary byproducts, allowing the formation of long, high-molecular-weight PLA chains useful for biodegradable manufacturing.

**Final Answer:** Ring-opening polymerization of cyclic lactide intermediate

**Answer:** (C)

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## Answer Key

Q	Ans	Q	Ans	Q	Ans	Q	Ans	Q	Ans
1	B	2	B	3	C	4	B	5	B
6	B	7	B	8	A	9	B	10	B
11	C	12	A	13	A	14	A	15	B
16	A	17	A	18	A	19	A	20	B
21	B	22	B	23	A	24	A	25	B
26	A	27	A	28	C	29	B	30	A
31	A	32	A	33	A	34	A	35	A
36	A	37	A	38	A	39	A	40	C

